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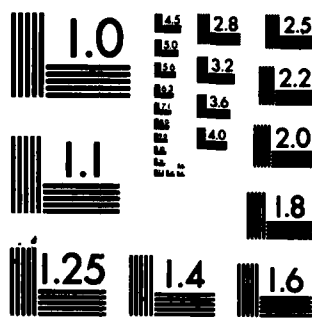
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FINAL REPORT, MARCH 1984

Anomalies in, and Crystallization of
Supercooled Water and Aqueous Solutions

by

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March 1984

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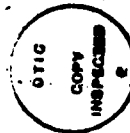
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these solutions, and also dielectric relaxation studies, have been performed. Spectroscopic measurements in both the far infrared and the near infrared, have yielded information on vibrational modes and characteristic hydrogen bonding structures. All together these measurements have done much to elucidate the anomalous behavior of water in the supercooled regime. They have served as the basis of two major invited reviews in the subject. In a separate branch of work, the nucleation of ice from aqueous solutions by a homogeneous mechanism has been subject to detailed examination and new insight into the mechanism into this important phase change has been obtained.

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FINAL REPORT

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ABSTRACT

This report summarizes research work performed under ONR auspices during the period 1978-1983. Thermodynamic studies of pure water and various aqueous solutions containing simple molecular second components such as H_2^{17}O , $\text{N}_2^{15}\text{H}_4$ and formamide have been performed at temperature down to -120°C , in order to perform extrapolations to obtain properties of (normal) water, i.e. water free from anomalous structure fluctuations. Properties studied have been heat capacity, expansivity and compressibility. On certain of these solutions viscosity, and also dielectric relaxation studies have been performed. Spectroscopic measurements in both the far infrared, and the near infrared, have yielded information on vibrational modes and characteristic hydrogen bonding structures. All together these measurements have done much to elucidate the anomalous behavior of water in the supercooled regime. They have served as the basis of two major invited reviews in the subject. In a separate branch of work, the nucleation of ice from aqueous solutions by a homogeneous mechanism has been subject to detailed examination and new insight into the mechanism into this important phase change has been obtained.

March 8, 1984

INTRODUCTION

The study of water in the metastable region below the normal freezing point has become a subject of widespread interest since the significance of early observations of physical properties in this regime was pointed out by the author and co-worker, R. J. Speedy. Speedy and Angell suggested that the anomalies of supercooled water were associated with a singularity for the substance which falls at -45°C at normal pressure and increasingly lower temperatures at higher pressures. The suggestion was made that the properties of water in this regime followed critical-type laws. A major part of the work undertaken under ONR support has been to refine these ideas and obtain suitable experimental data for testing the critical law behavior. The thrust of the work has been largely to use binary solutions in which the anomalous characteristics of water are damped out by the addition of second components to extract, by extrapolation procedures, the anomalous part of each property of water, this being a part which might be expected to exhibit critical law behavior.

In addition to the study of the intrinsic behavior of the liquid state, interest also resides in the manner in which the supercooled state is terminated by crystallization, normally of ice(I). Part of our effort has gone into characterizing the process of nucleation and growth of ice from metastable solutions in which we can control the kinetics of the process by controlling the binary solution composition.

March 8, 1984

TECHNIQUES USED AND RESULTS

Thermodynamic Studies

Pure water. The heat capacity of pure water has been determined in a careful refinement of our earlier work by two separate investigators using two different versions of the emulsion technique. These investigators obtained, using differential scanning calorimetry of small emulsion samples, data which agreed with each other to within 1.5% over the whole temperature range, and with literature data within 1% in the common temperature range. These results were published in the Journal of Physical Chemistry in a paper combining observations on supercooled and superheated properties (see Appendix I).

Solution Studies. The heat capacities of solutions in the systems $\text{H}_2\text{O} + \text{H}_2\text{O}_2$, and of $\text{H}_2\text{O} + \text{N}_2\text{H}_4$, were determined by both emulsion differential scanning calorimetry in dilute solutions, and bulk sample DSC for concentrated solutions. Results were used to extrapolate an anomalous component, as distinguished from normal behavior defined by the extrapolation, for pure water. The behavior of the anomalous component was analyzed using critical laws to obtain the characteristic parameters of the critical behavior. Results were published in the Journal of Chemical Physics (see Appendix II).

In the binary system $\text{H}_2\text{O} + \text{formamide}$ (HCONH_2), expansivity and compressibility measurements, in addition to heat capacity measurements, were performed in order to check for consistency of singular parameters from other thermodynamic properties. The PVT

March 8, 1984

properties were determined using thin capillary techniques. Data of high accuracy were obtained by M. Oguni, and results and conclusions were published in J. Chem. Phys. (see Appendix III).

Vapor deposited vitreous water. In order to characterize the vitreous state of water, and attempt to obtain a glass transition temperature, D. R. MacFarlane made deposits of water vapor in amorphous form directly into a differential scanning calorimeter pan. This was then transferred to the DSC and warm-up characteristics determined. A sharp crystallization was observed at 167 K, as had been reported by previous workers, but despite the use of very high sensitivity, no trace of a glass transition was found at the temperature expected from binary solutions. These results and their interpretation have been published in the Journal of Physical Chemistry (see Appendix IV).

Time Dependent Properties

Viscosity studies. M. Oguni, using a capillary viscometer technique performed measurements of viscosity on $H_2O + \text{formamide}$, and $H_2O + N_2O_4$, binary solutions at temperatures down to -30°C in order to obtain data with which to perform similar extrapolations to those above in order to obtain normal and anomalous components of this transport property for water. Results and interpretation, which have not yet been published, are contained in preprint form in Appendix V.

Dielectric relaxation studies. In order to characterize the direct relaxational character of water in its binary solutions, a series of measurements were made on binary solutions of water and

propylene glycol, which can be supercooled into the high viscosity region over composition ranges which are unusually wide. These measurements were performed, using a small all metal three terminal cell by D. L. Smith and have been combined with a far infrared vibrational spectrum study of the same solutions (see below) for publication. The manuscript, see Appendix VI, will be submitted to the Journal of Chemical Physics.

Spectroscopic Studies

Far infrared spectra. A short study of these spectrum of pure water and water + propylene glycol solutions was performed by Dr. L. Boehm in order to obtain information on the behavior of low frequency modes which might play the role of the attempt mode for relaxational properties of water and solutions. This work was performed using thin films of water or solutions sandwiched between densified polyethylene windows cooled in the chamber of Digilabs far IR spectrophotometer. The results are incorporated in the manuscript, Appendix VI, referred to in the last section.

Near IR spectra of aqueous solutions and microemulsions. In the most recent project conducted under ONR support, a newly acquired Cary-17DHC UV visible IR spectrophotometer has been used to study the overtone spectra of water in two different, and to an extent novel situations, by D. L. Fields. The first study has been on water contained in the newly developed microemulsions in which there is no co-surfactant, but instead only the three components, water, decane, and the surfactant di-dodecyl dimethyl ammonium bromide. The special feature of this microemulsion is

March 8, 1984

that the only-OH groups present derive from the water component. Our interest in this subject has been two-fold. (1) To obtain information on the structure of water in the microemulsion form, (2) attempt to use the microemulsion state as a novel manner of reaching low, sub-freezing temperatures. Only the first of these aims has been realized, though measurements on microemulsion state of water to lower temperatures than ever before have in fact been obtained. The spectra obtained have resembled those of a dilute alkali bromide solution except for the presence of three sharp peaks corresponding to OH overtone vibrations which presumably belong to water molecules at the micell edge. This work has not yet been completed.

The second study has been designed to yield information on "free" OH vibrations in solutions where the "free" OH groups have been produced by a sort of chemical titration procedure. Basically binary solutions of hydrazine N_2H_4 and water are prepared and characterized spectroscopically, to reveal the overtones of the non-hydrogen bonded N-H groups which are present in excess of the number of nitrogen lone pairs to which they can hydrogen bond. These free N-H groups are then titrated by addition of perchloric acid which creates $N_2H_5^+$ cations in which the protons are now sufficiently acid that they seek lone pairs to which to hydrogen bond at the expense of protons deriving from the water molecules present. This, in principle, sets free an equivalent number of "free" OH groups whose overtone spectra are then revealed.

March 8, 1984

A systematic study of these solution spectra has now been performed at ambient temperature, and the measurements are now being extended to lower temperatures. An initial surprise has been the finding that, at the stoichiometric N_2H_5 composition, decrease of temperature, instead of leading to a sharpening of the "free" OH spectrum, results in its diminution. Evidently the thermal disruption of hydrogen bonded groups is still the major factor determining the concentration of "free" OH groups in this solution. It remains to create solutions which can be supercooled to much lower temperatures in order to see whether the chemically created free OH's can be obtained as residual spectral characteristics at low temperatures. We believe this study to be novel amongst attempts to characterize hydrogen bonding structures in aqueous systems.

Most of the foregoing research has been described, along with that of other workers, in the first review of the field of supercooled water by Annual Reviews of Physical Chemistry, see Appendix VII.

Nucleation and Growth of Ice From Supercooled Aqueous Solutions

The study of ice crystallization phenomena was commenced in this laboratory under NSF auspices, but was transferred to ONR support when this was extended in 1982. The ONR-supported part of this research has been focussed on the use of differential scanning calorimetry to monitor the crystallization process as it occurs during different isothermal observations. The work was performed principally by K. Kadiyala, a talented undergraduate

March 19, 1984

student who worked as a summer research assistant on this project, and has continued part time during the academic year. This work has been remarkably successful, insofar as it led to the first direct observation of the classical time-temperature-transformation curves, and has since been developed into a tool for separating those parts of the crystallization phenomenon which are dominated by the kinetics of the nucleation process, from those parts which are dominated by the growth of nuclei to microscopic crystals.

The basic studies have been concentrated on the binary system water + LiCl, this electrolyte solution being chosen because of its use in initial studies of the crystallization process using neutron scattering techniques.

The work is described in three publications, Appendices VIII, IX, X and XI appearing or to appear, in Journal of Physical Chemistry (Appendix VII and VIII), Journal of Chemical Physics (Appendix IX) and Journal of Colloids and Interfaces (Appendix X). The last of these is a manuscript which reports our first work using the new two step isothermal calorimetry technique, and was solicited for an international conference on crystallization held at Cambridge, England this past summer. We expect this technique to be widely used in future studies of nucleation and growth phenomena.

March 19, 1984

APPENDIX

- I. "Heat Capacity of Water at Extremes of Supercooling and Superheating," C. A. Angell, W. J. Sichina and M. Oguni, J. Phys. Chem. 86, 998 (1982).
- II. "Volumetric and Derived Thermal Characteristics of Liquid $\text{HO} + \text{H}_2\text{O}_2$, and $\text{HO} + \text{N}_2\text{H}_4$, Binary Solutions; Isolation of a Singular Component for C of Supercooled Water," M. Oguni and C. A. Angell, J. Chem. Phys. 73, 1948 (1980).
- III. "Anomalous Components of Supercooled Water Expansivity, Compressibility and Heat Capacity (C_p vs. C_v) from Binary Formamide + Water Solution Studies," M. Oguni and C. A. Angell, J. Chem. Phys 78(12), 7334 (1983).
- IV. "On the Glass Transition for Amorphous Water," D. R. MacFarlane and C. A. Angell, J. Phys. Chem., Feb. '83 (in press).
- V. "'Normal" and "Anomalous" Components of the Viscosity of Supercooled Water from Binary Solutions with HCONH_2 ," M. Oguni and C. A. Angell, J. Phys. Chem. (to be submitted).
- VI. "Far Infrared and Dielectric Relaxation Spectra in Supercooled Water and Water + Propylene Glycol Solutions," L. Boehm, D. L. Smith and C. A. Angell, J. Phys. Chem. (to be submitted).
- VII. "Supercooled Water," by C. A. Angell, Ann. Revs. Phys. Chem. 34, 593 (1983).

March 19, 1984

Curves for Crystallization of Ice from Solution
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IX. (a) "The Cooling Rate Dependence of the Ice I Nucleation
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J. Chem. Phys. 78(8), 3821 (1983).

XI. "Separation of Nucleation from Crystallization Kinetics by
Two Step Calorimetry Experiments," R. K. Kadiyala and C. A. Angell,
J. Colloids and Interfaces (in press).

March 19, 1984

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